

About the polymerization of aromatic compounds under atmospheric plasma conditions

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Plasma polymerization of aromatic compounds was studied using a dielectric barrier discharge in helium, working at atmospheric pressure. The chemical composition and structure of polymerized films were obtained by means of infrared spectroscopy, X-ray photoelectron spectroscopy and nuclear magnetic resonance spectroscopy. The correlation between the spectroscopic techniques allows to develop a plasma polymerization mechanism from a chemical point of view.

Plasma polymerization is a physical procedure in which mostly chemical reactions are involved. The organic vapors are activated and fragmented under the influence of plasma energy and the new created reactive species are randomly recombined into high branched and crosslinked structures. The final compounds are conventionally called plasma polymer films. Organic compounds developed by plasma polymerization contains some physical properties that make them unique in all types of polymers. Plasma polymers developed by gas discharges are mechanical and thermal stable coatings, chemically inert, they are adherent to almost all substrate types, could be deposited onto thin layers with controllable thickness and could be synthesized from a wide range of starting precursors. The chemical structure of coatings depend on chemical properties of starting monomer but also it depends by physical parameters of electrical discharge such as working pressure, discharge power, electrodes configuration and design etc. The properties of plasma polymers are, therefore, different from those obtained by conventional polymerization. Polymerized films are used in many applications such as optical devices, biomaterials, protective coatings, electrical insulators, conductive and permselective membranes [1].

In order to control the properties of polymerized films, it is necessary to study the intermediar reactions during plasma polymerization. In this way, some mechanisms of polymerization were proposed from physical and chemical point of view.

From physical point of view, Neiswender proposed an energy-related factor in order to identify different regimes of plasma polymerization reactions [2]. This idea was improved by Yasuda, who evaluated the composite parameter, W/FM, with W the discharge power, F the monomer flow rate and M the molecular weight of monomer[3]. The discharge power per unit of molecule is considered to be proportional with the concentration of activated species in plasma. Hegemann et al developed a macroscopic approach to control plasma polymerization processes[4]. They "divided" the plasma zone into two different regions. In the active plasma region, the organic molecules are activated or fragmented, reactive species which then recombines, followed by reactivation and poly-recombination of reaction products. The passive plasma region is considered evidenced at the substrate vicinity, where the recombination reactions, ablation and re-deposition processes occur.

They are many studies related to plasma polymerization mechanism from chemical point of view. Stille suggested a model for plasma reactions of benzene [5], Tibbitt investigated the structure of plasma-polymerized ethylene [6], Kaplan studied the polymerization reactions of aromatic compounds [7] etc.

The aim of the present study is the development of a plasma polymerization mechanism using different aromatic precursors: benzaldehyde, benzyl alcohol, styrene and benzyl chloride. The polymerized films were investigated by means of Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and proton nuclear magnetic resonance (¹H NMR). The spectroscopic techniques allow us to identify the chemical structure of final compounds and, consequently, the intermediar reactions during plasma polymerization processes.

A dielectric barrier discharge working in helium was used for the deposition of thin polymeric films. The experimental set-up and the operational parameters were described in our previous work

[8]. The aromatic precursors were introduced into the discharge chamber by gas bubbling and the total flow rate (helium + organic vapours flow rate) was maintained at 2.5 L/min.

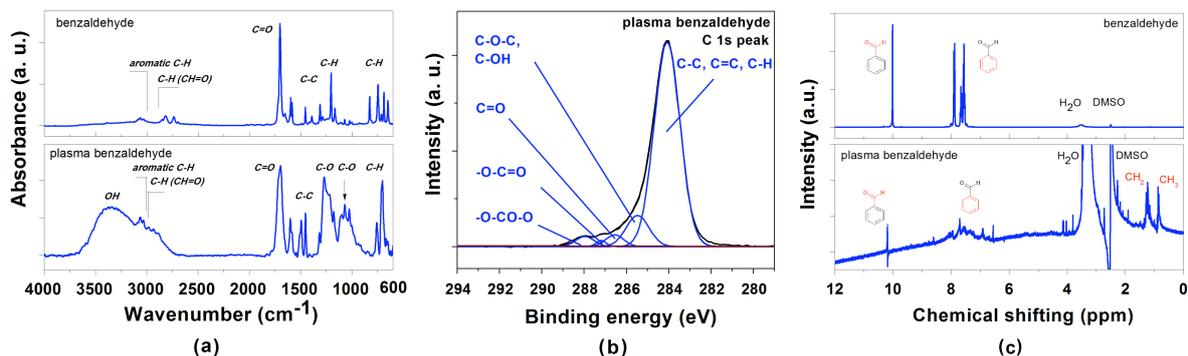


Fig. 1: a) FT-IR spectra, b) XPS spectrum, c) ^1H NMR spectra of benzaldehyde and plasma benzaldehyde, respectively.

The FT-IR spectra indicate the chemical structure of plasma polymerized films. The absorption peaks are assigned to chemical groups from initial molecules but also from reactive species fragmented or activated due to plasma exposure (Fig. 1a). The FT-IR spectrum of plasma polybenzaldehyde shows a broad band around 3300 cm^{-1} corresponding to hydroxyl groups, as the effect of oxidation during plasma polymerization. The aldehydic region from $2910 - 2670\text{ cm}^{-1}$ is shifted up to 3000 cm^{-1} suggesting that CH group from $\text{CH}=\text{O}$ is now of aliphatic or alcohol type by aldehyde reduction in plasma environment. New peaks at 1265 cm^{-1} and 1068 cm^{-1} are specific to C-O-C and C-O, respectively, confirming that carbon-oxygen π bond from aldehyde can be broken.

The XPS spectra estimate the chemical composition of final compounds and, also, provide informations about the oxidation reactions that occur due to atmospheric impurities. Typical XPS spectrum of plasma polybenzaldehyde (fig. 1b) indicates the presence of 83.3 % carbon and 16.7 % oxygen. The fitted C 1s spectrum contains five distinctive components assignable to C-H, C-C and C=C (284.1 eV), ether C-O-C and alcohol C-OH groups (285.5 eV), carbonil C=O type bonds (286.6 eV), esters -O-C=O (287.2 eV) and O-CO-O of carbonate group (288 eV).

The NMR spectra reveal complementary informations about the chemical structure of final compounds. The ^1H -NMR spectrum of plasma benzaldehyde includes the signal specific to aldehydic proton and a broad band corresponding to aromatic protons that indicates the presence of intact monomer molecules in the final compound. Now these signals have a smaller intensity and the aromatic protons are more dispersed causes overlap of the signals. New peaks of aliphatic protons are detected in the ^1H NMR spectrum of final compound. Thus, the chemical shifting from 1.24 ppm is specific to methylene CH_2 protons and the 0.88 ppm peak corresponds to methyl CH_3 protons of aliphatic type. The two peaks at 4.15 ppm are specific to methylene CH_2 protons attached to the benzene ring. However, the above mentioned signals provide informations about the fragmentation processes.

Similar discussions were performed for plasma polymerization of benzyl alcohol, styrene and benzyl chloride. The chemical mechanism of plasma polymerization process combines the results of all spectroscopic analysis; however, during plasma polymerization of aromatic precursors we identified the activation and fragmentation reactions, oxidation reactions and poly-recombination of reactive species into randomly structures like three-dimensional polymeric networks.

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